CLAIMS

What is claimed is:

1. A process for producing a block copolymer, comprising:

   heating styrene and an unsaturated cyclic anhydride (UCA) in the presence of a free radical initiator and a stable free radical at temperatures between about 110 and about 200°C, adjusting or setting the ratio of initiator to monomer in order to control the total length of the chain, cooling the reaction mixture; and recovering a block copolymer by isolating the block copolymer from un-reacted monomer, wherein the composition of the block copolymer comprises:

   a first block comprising a random copolymer of styrene and unsaturated cyclic anhydride having a total length between about 1 and about 720 monomeric units; and

   a second block comprising an essentially pure polystyrene block having a length between about 100 and about 2000 monomeric units, wherein

   the polydispersity is between about 1.2 and about 3.

2. The process of claim 1, wherein the first block has some degree of alternating character given by the reactivity ratios of the monomers.

3. The process of claim 1, wherein the number average molecular weight of the chain is controlled by adjusting or setting the molar concentration of initiator to a value of about

   A - ($5x10^{-8}$ Mn) if the desired molecular weight is larger than about 61500, and

   B - ($3.33x10^{-7}$ Mn) if the desired molecular weight is smaller than about 61500,

wherein Mn is a target value for number average molecular weight; A is between about 0.005 and about 0.01; and B is between about 0.016 and about 0.042.

4. The process of claim 1, wherein the value of the molar ratio of stable free radical to initiator is at least about

   1.3 + 0.10 * (weight percentage of UCA with respect to total monomers).

5. The process of claim 1, wherein the UCA is maleic anhydride.

6. The process of claim 1, wherein the UCA is itaconic anhydride.

7. The process of claim 1, wherein the temperature range is between about 120 and about 170 °C.

8. The process of claim 1, wherein the temperature range is between about 120 and about 150°C.

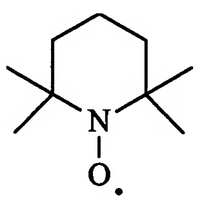
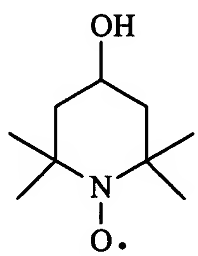
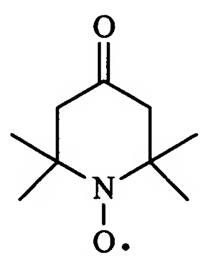
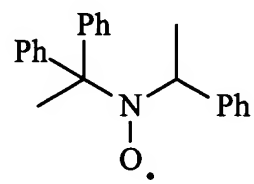
9. The process of claim 1, wherein the proportion of UCA in the mixture styrene – UCA is in the range of about 0.09 to about 18 % by weight.

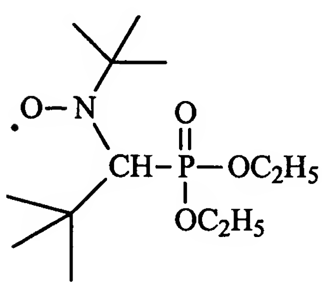
10. The process of claim 1, wherein the proportion of UCA in the mixture styrene – UCA is in the range of about 0.3 to about 10 % by weight.

11. The process of claim 1, wherein the proportion of UCA in the mixture styrene – UCA is in the range of about 0.9 to about 8 % by weight.

12. The process of claim 1, wherein the stable free radical is a nitroxyl free radical.

13. The process of claim 12, wherein the nitroxyl free radical is selected from the group consisting of:



14. The process of claim 1, wherein the free radical initiator is selected from the group consisting of:

2,2'-Azobis (2 -Methylpropanenitrile), 2,2'-Azobis (2-Methylbutanenitrile), dibenzoyl peroxide (BPO), Tert-Amyl peroxy-2-ethylhexanoate, Ter-Butyl peroxy-2-ethylhexanoate, 2,5-Bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane and ter-Butyl peroxydiethylacetate.

15. A process for producing a block copolymer, comprising:

heating styrene and an unsaturated cyclic anhydride in the presence of a free radical initiator and 6-hydroxy 2,2,6,6 tetramethyl-piperidine-N-oxyl and/or 6-oxo 2,2,6,6

tetramethyl-piperidine-N-oxyl stable free radical at temperatures between about 110 and about 200°C;

cooling the reaction mixture; and recovering a block polymer by isolating the block copolymer from non-reacted monomer.

16. The process of claim 15, wherein the number average molecular weight of the chain is controlled by manipulating the molar concentration of initiator to have a value of about

$A - (5x10^{-8}\ Mn)$ if the desired molecular weight is larger than about 61500, and

$B - (3.33x10^{-7}\ Mn)$ if the desired molecular weight is smaller than about 61500,

in which Mn is a target value for number average molecular weight; A is between about 0.005 and about 0.01 and B is between about 0.016 and about 0.042.

17. A process for producing a block copolymer, comprising:

heating styrene monomer and an unsaturated cyclic anhydride monomer to a temperature range between about 110 and about 200°C in a reactor;

adding a free radical initiator to the reactor;

adding a stable free radical to the reactor; and

recovering a block copolymer, wherein a desired molecular weight range of the block copolymer is obtained by manipulating or adjusting or setting the molar ratio of free radical initiator to total monomer.

18. The process of claim 17, wherein the process is continuous.

19. The process of claim 17, further comprising providing a molar ratio of stable free radical to initiator of about:

1.3 + 0.10 * (weight percentage of unsaturated cyclic anhydride with respect to total monomers).

20. The process of claim 17, wherein the number average molecular weight of the chain is controlled by setting the molar concentration of initiator to about

A minus $(5x10^{-8})$ times Mn, if the desired molecular weight is larger than about 61500, and

B minus $(3.33x10^{-7})$ times Mn if the desired molecular weight is smaller than about 61500,

where Mn is a desired number average molecular weight; A is between about 0.005 and about 0.01; and B is between about 0.016 and about 0.042.

21. A process comprising:

heating styrene and unsaturated cyclic anhydride in the presence of a solvent, a free radical initiator and a stable free radical to a temperature ranging between about 110 and about 200 °C for more than about two hours.

22. The process of claim 21, wherein the pressure of the process is adjusted to be above the vapor pressure of the reaction mixture.

23. The process of claim 21, wherein the pressure of the process is adjusted to be about equal to or above that given by the formula

$2.5\ P_0\ x_s$, if x_s is less than about 0.2 or

$1.4\ P_0\ x_s$, if x_s is equal to or greater than about 0.2,

where P_0 is the vapor pressure of the solvent at the temperature of the reaction, and x_s is the mole fraction of solvent in the mixture of solvent and monomer.

24. The process of claim 21, wherein the solvent is ethyl acetate, toluene, chloroform, xylene, acetone and/or ethyl benzene.

25. The process of claim 21, wherein the solvent is present in an amount of 10-95 % by weight on the basis of the mixture of monomers and solvent.

26. The process of claim 21, wherein the solvent is present in an amount of 10-30 % by weight on the basis of the mixture of monomers and solvent.

27. The process of claim 21, wherein the solvent is present in an amount of 15-25 % by weight on the basis of the mixture of monomers and solvent.

28. The process of claim 21, wherein the solvent is present in an amount of 60-95 % by weight on the basis of the mixture of monomers and solvent.

29. The process of claim 21, wherein the solvent is present in an amount of 70-90 % by weight on the basis of the mixture of monomers and solvent.

30. The process of claim 21, wherein the solvent is present in an amount of 75-88 % by weight on the basis of the mixture of monomers and solvent.

31. A process for producing a block copolymer, comprising:

heating to a temperature range between about 110 and about 200°C in a reactor styrene monomer and an unsaturated cyclic anhydride monomer wherein the

proportion of unsaturated cyclic anhydride in the mixture styrene – unsaturated cyclic anhydride is in the range of about 0.09 to about 18 wt. %;

adding a free radical initiator to the reactor in a molar ratio of monomer to initiator of about 100 to about 12000 ;

adding TEMPO or a derivative of TEMPO to provide a stable free radical resulting in a ratio of stable free radical to initiator of about 1.0 to about 3.0;

cooling the reaction mixture; and

recovering a block copolymer by isolating the block copolymer from un-reacted monomer, the block copolymer having a molecular weight greater than about 25,000.

32. The process of claim 31, wherein the molecular weight of the block copolymer is between about 50,000 and about 100,000.

33. The process of claim 31, wherein a solvent is added to the reaction mixture.

34. A process for producing a block copolymer, comprising the steps of:

mixing styrene and an unsaturated cyclic anhydride in the presence of a solvent;

adding a free radical initiator to the mixture in a molar ratio of monomer to initiator of about 100 to about 12000;

adding as stable free radical 6-hydroxy 2,2,6,6 tetramethyl-piperidine-N-oxyl and/or 6-oxo 2,2,6,6 tetramethyl-piperidine-N-oxyl;

using a molar ratio of stable free radical to initiator of about

1.3 plus about 0.10 times (weight percentage of UCA with respect to total monomers),

wherein the weight percentage of UCA with respect to total monomers is between about 0.1 and about 16%.

35. The process of claim 34, further comprising cooling the reaction mixture and recovering a block copolymer having a molecular weight greater than about 35,000.

36. A process for controllably producing a block copolymer having a molecular weight greater than about 30,000 using living free radical polymerization, comprising the steps of:

maintaining styrene and an unsaturated cyclic anhydride (UCA) in a reactor at temperatures between about 110 and about 200°;

adding a free radical initiator to the reactor in a molar ratio of monomer to initiator of about 100 to about 12000; and

adding a stable free radical at a molar ratio of stable free radical to initiator of about 1.3 plus 0.25 times (weight percentage of UCA with respect to total monomers),

the weight percentage of UCA with respect to total monomers being between about 0.1 and about 6 %.

37. The process of claim 36, wherein the stable free radical comprises 6-hydroxy 2,2,6,6 tetramethyl-piperidine-N-oxyl and/or 6-oxo 2,2,6,6 tetramethyl-piperidine-N-oxyl.

38. A process for producing a block copolymer, comprising:

reacting styrene monomer and an unsaturated cyclic anhydride monomer in the presence of a free radical initiator and a stable nitroxyl free radical and with (or without) a solvent with some polarity at temperatures between about 110 and about 200°C; and

recovering a block copolymer, wherein the composition of the block copolymer comprises:

a first block comprising a random copolymer of styrene and an unsaturated cyclic anhydride, with some degree of alternating character given by the reactivity ratios of the monomers, and a total length between about 1 and about 720 monomeric units; and

a second block comprising an essentially pure polystyrene block having a length between 100 and 2000 monomeric units, wherein

the polydispersity is between about 1.2 and about 3.0.

39. The process of claim 38, wherein the molar ratio of nitroxyl radical to initiator is between about 1.3 and about 3.0.

40. The process of claim 38, wherein the molar ratio of nitroxyl radical to initiator is between about 1.6 and about 2.5.

41. The process of claim 38, wherein the molar ratio of nitroxyl radical to initiator is between about 1.9 and about 2.5.

42. The process of claim 38, wherein the molar ratio of total monomer to initiator is in the range of about 100 to about 12,000.

43. The process of claim 38, wherein the molar ratio of total monomer to initiator is in the range about 200 to about 3,000.

44. The process of claim 38, wherein the molar ratio of total monomer to initiator is in the range about 600 to about 1,500.

45. A process for making a copolymer, comprising:

heating styrene and an unsaturated cyclic anhydride in the presence of a free radical initiator and a stable free radical at temperatures between about 110 and about 200°C;

agitating the reactants in a first reactor until a conversion of about 10 to about 50 % is obtained;

maintaining the reactants in the first reactor or in a second reactor, without agitation, until a conversion of about 90 to about 100 % is obtained; and

recovering a block copolymer, wherein the composition of the block copolymer comprises:

a first block comprising a random copolymer of styrene and an unsaturated cyclic anhydride, having a total length between about 1 and about 720 monomeric units; and

a second block comprising nearly pure polystyrene block having a length between about 100 and about 2000 monomeric units.

46. The process of claim 45, wherein the block copolymer has a polydispersity between about 1.2 and about 3.0.

47. The process of claim 45, wherein the unsaturated cyclic anhydride is maleic anhydride.

48. The process of claim 45, wherein the unsaturated cyclic anhydride is itaconic anhydride.

49. A process for making a copolymer, comprising:

reacting styrene and an unsaturated cyclic anhydride in the presence of a free radical initiator and a stable free radical to form a reaction mixture; and

recovering a block copolymer, wherein the composition of the block copolymer comprises:

a first block comprising a random copolymer of styrene and an unsaturated cyclic anhydride having a total length between about 1 and about 720 monomeric units; and

a second block of mostly polystyrene having a length between 100 and 2000 monomeric units, further comprising:

a) heating and passing the reaction mixture through a tubular type reactor in which the exit fractional monomer conversion is numerically about twice or larger than the mass fraction of UCA in the feed (with respect to total monomer) to form a first intermediate;

b) passing the first intermediate into a continuous stirred tank reactor with exit conversions between about 10 and about 50 % weight to form a second intermediate; and

c) passing the second intermediate through a tubular type reactor in which the final conversion is between about 60 and about 100 % by weight.

50. The process of claim 49, wherein step (a) is omitted and the first intermediate referred to in step (b) is fresh feed.

51. The process of claim 49, wherein the unsaturated cyclic anhydride is maleic anhydride.

52. The process of claim 49, further comprising recovering and recycling unreacted styrene monomer.

53. A process comprising:

forming a reaction mixture by heating styrene and unsaturated cyclic anhydride in the presence of a solvent, a free radical initiator and a stable free radical to a temperature ranging between about 110 and about 200°C in steps including:

a) heating and passing the reaction mixture through a first tubular type reactor in which the exit fractional monomer conversion is numerically about twice or larger than the mass fraction of UCA in the feed (with respect to total monomer) to form a first intermediate; and

b) heating the reaction mixture in a continuous stirred tank reactor with exit monomer conversion between about 10 and about 50 % to form a second intermediate; and

c) passing the second intermediate through a second tubular type reactor in order to get an exit monomer conversion between about 60 and about 100 % by weight.

54. The process of claim 53, wherein the step (a) is omitted and the reaction mixture referred to in step (b) is fresh feed.

55. The process of claim 53, wherein the second tubular type reactor is a vertical plug-flow reactor fed by the bottom.

56. The process of claim 53, wherein the solvent is toluene, acetone, ethyl acetate, xylene and/or ethyl benzene.

57. The process of claim 53, wherein the unsaturated cyclic anhydride is maleic anhydride.

58. The process of claim 53, wherein the unsaturated cyclic anhydride is itaconic anhydride.

59. A block copolymer composition, comprising:

a) a first block comprising random copolymer of styrene and an unsaturated cyclic anhydride having a total length between about 1 and about 720 monomeric units; and

b) a second block comprising an essentially pure polystyrene block having a length between 100 and 2000 monomeric units, wherein

c) the polydispersity is between about 1.2 and about 3.0.

60. The composition of claim 59, wherein the first block has some degree of alternating character given by the reactivity ratios of the monomers.

61. The composition of claim 59, wherein the polystyrene block contains a covalently bonded nitroxyl terminus of only one chemical formula.

62. The block copolymer of claim 59, wherein the unsaturated cyclic anhydride is maleic anhydride.

63. The block copolymer of claim 59, wherein the unsaturated cyclic anhydride is itaconic anhydride.

64. A block copolymer, comprising:

a block of a copolymer of styrene and an unsaturated cyclic anhydride; and

a block of polystyrene having a length between about 100 and about 2000 monomeric units, wherein

the polydispersity is between about 1.2 and about 3.0.

65. The copolymer of claim 64, wherein the block of a copolymer of styrene and an unsaturated cyclic anhydride has a length of between about 1 and about 720 monomeric units.

66. A method for compatibilization of an engineering thermoplastic with a thermoplastic polymer that is compatible or miscible with polystyrene, comprising: mixing the two polymers together in relative proportions with a block copolymer of styrene and unsaturated cyclic anhydride monomer in a reaction vessel, wherein the block copolymer is made by a process comprising heating to a temperature range between about 110 and about 200°C in a reactor styrene monomer and an unsaturated cyclic anhydride monomer; adding a free radical initiator to the reactor; adding a stable free radical; manipulating or adjusting or setting the molar ratio of free radical initiator to total monomer; and recovering a block copolymer.

67. The method of claim 66, wherein the reaction vessel is an extruder.

68. A thermoplastic polymer composition, comprising:

(a) 1- 98 wt % engineering thermoplastic having functional groups capable of reacting with or compatible with styrene and an unsaturated cyclic anhydride block copolymer

(b) 1- 98 wt % thermoplastic polymer with polymer segments compatible or miscible with the polystyrene block of the block copolymer; and

(c) 1-20 wt % of the block copolymer.

69. The composition of claim 68, wherein the block copolymer is made by the process of claim 1.

70. A thermoplastic polymer composition, comprising:

(a) 1-98 wt % engineering thermoplastic having a functional group selected from the group consisting of amino (NH2), amide (NH), carboxyl (COOH) and hydroxyl (OH)

(b) 1-20 wt % styrene maleic anhydride block copolymer; and

(c) 1-98 wt % thermoplastic polymer miscible or compatible with the polystyrene block in the styrene-maleic anhydride block copolymer.

71. The composition of claim 70, wherein the block copolymer is made by the process of claim 1.

72. The thermoplastic polymer composition of claim 70, wherein the molecular weight of the styrene-maleic anhydride block copolymer ranges between about 10,000 and about 200,000.

73. The thermoplastic polymer composition of claim 70, wherein the styrene-maleic anhydride block copolymer comprises between about 0.1 and about 18 weight percent maleic anhydride.

74. The composition according to claim 70, wherein the engineering thermoplastic polymer is selected from the group consisting of: aliphatic or aromatic polycarbonates, polyesters, polyamides, polyphenylene ether, and mixtures thereof.

75. The composition according to claim 70, wherein the thermoplastic polymer is high impact polystyrene.

76. The composition according to claim 70, wherein the thermoplastic polymer is a block copolymer of styrene and butadiene.

77. The composition according to claim 70, wherein the engineering thermoplastic is a polyamide and the thermoplastic polymer is polyphenylene ether, alone or in mixtures with polystyrene and/or high impact polystyrene and/or a styrene-butadiene block copolymer.

78. The composition according to claim 70, wherein the engineering thermoplastic is a polyamide and the thermoplastic polymer is high impact polystyrene and/or a styrene-butadiene block copolymer.

79. The composition according to claim 70, wherein the thermoplastic polymer is a styrene-methyl methacrylate copolymer.

80. The composition according to claim 70, wherein the engineering thermoplastic is an aromatic polycarbonate and the thermoplastic polymer is polystyrene and/or high impact polystyrene and/or styrene-butadiene block copolymer.

81. The composition according to claim 70, wherein the engineering thermoplastic is a polyethylene terephtalate and the thermoplastic polymer is polystyrene and/or high impact polystyrene and/or a styrene-butadiene block copolymer.

82. The composition according to claim 70, wherein the engineering thermoplastic is a polybutylene terephtalate and the thermoplastic polymer is polystyrene and/or high impact polystyrene and/or a styrene-butadiene block copolymer.

83. A method for making a polymer composition, comprising:

mixing a thermoplastic polymer compatible or miscible with polystyrene and a filler together in relative proportions with a block copolymer of styrene and unsaturated cyclic anhydride monomer in a reaction vessel, wherein the block copolymer is made by a process comprising heating to a temperature range between about 110 and about 200°C in a reactor styrene monomer and an unsaturated cyclic anhydride monomer; adding a free radical initiator to the reactor; adding a stable free radical; manipulating or adjusting or setting the molar ratio of free radical initiator to total monomer; and recovering a block copolymer.

84. The method of claim 83, wherein the reaction vessel is an extruder.

85. A thermoplastic polymer composition, comprising:

(a) 40-98 wt % thermoplastic polymer with polymer segments compatible or miscible with the polystyrene block of a styrene-maleic anhydride block copolymer;

(b) 1-40 wt% of a filler containing functional moieties that show strong chemical affinity or can react with the dicarboxylic moiety of the styrene-maleic anhydride block copolymer; and

(c) 1-20 wt % styrene - unsaturated cyclic anhydride block copolymer.

86. The composition of claim 85, wherein the styrene-unsaturated cyclic anhydride block copolymer is made by the process of claim 1.

87. The composition according to claim 85, wherein the thermoplastic polymer is polystyrene and/or high-impact polystyrene and/or a styrene-butadiene block copolymer.

88. The composition according to claim 87, wherein the filler is fiber glass.